Composite materials glassy carbon/graphene/zero-valent metal (Pd0) for building three-dimensional redox electrodes

Viatcheslav Jouikov, Jacques Simonet

Electrochemistry Communications 42 (2014) 34–37

Contents lists available at ScienceDirect

Electrochemistry Communications

journal homepage: www.elsevier.com/locate/elecom

Short communication

Composite materials {glassy carbon/graphene/zero-valent metal (Pd^0)} for building three-dimensional redox electrodes

Viatcheslav Jouikov [a], Jacques Simonet [b,*]

[a] UMR 6226 CPM, Université de Rennes 1, Campus de Beaulieu, 35042 Rennes Cedex, France
[b] Laboratoire MaSCE, UMR 6226, Université de Rennes 1, Campus de Beaulieu, 35042 Rennes Cedex, France

ARTICLE INFO

Article history:
Received 24 January 2014
Received in revised form 12 February 2014
Accepted 12 February 2014
Available online 19 February 2014

Keywords:
Graphene electrodes
Alkyl radical trapping
Chemically modified electrodes
Redox catalysis
Ferrocene grafting

ABSTRACT

When glassy carbon (GC) is mechanically covered with micrometric layers of graphene, the reduction of primary alkyl halides (RX) can shift to the catalytic mode due to the fact that cathodically charged graphene may act as a redox reducing agent triggering a classical redox catalytic process with a moderate gain (<0.2 V) in potential. Alternatively, the injection of very small amounts of transition metals (not only Pd, but also Au, Ag or Pt) at zero-valent state into the graphene layer may induce catalytic reduction of RIs and RBrs that allows the formation of free radicals R• and their concomitant grafting, not only at the GC/graphene interface but also in bulk graphene that plays the role of a three-dimensional radical scavenger. Therefore, by use of this simple process, GC/graphene layers could be converted into a 3D active interface. In order to quantify the global grafting/insertion of R•, ferrocene and aryl probes (Fc-*n*-alkyl-I and pyrene-CH_2-Br) were used, attesting to significant modification of the interface. Thus, for the first time, a bulky graphene–ferrocene layer (a redox system fully usable as a 3D modified electrode) was built. This model could quite hopefully be envisaged for electrochemically incorporating many other redox centers in graphene within the potential range of −2 V to +1 V vs. Ag/AgCl.

1. Introduction

The use of carbon electrodes remains quite general in electrochemistry. In particular, glassy carbon (GC) is often preferred as cathode material [1] due to its wide possibilities within both the anodic and the cathodic range. For reductions, it is preferred to metals (Cu, Pd, and Au) because of its reasonably good hydrogen over-potential value. GC was for long supposed to be a quite inert material, non-reactive towards the products of electrode reaction(s) and therefore considered as almost ideal material, especially when used for cathodic scission of carbon–halogen bonds [2]. Very recently, the addition of free aryl [3] and alkyl [4] radicals, issued from different cathodic scission reactions, onto glassy carbon permitted to (re)consider that GC was finally a composite material embedding graphite and fullerene-like nanoparticles. This material should hence be seen as endowed with dual chemical reactivity and able to act both as a radical trap and as an electroactive species (permitting the formation of carbon poly-nucleophiles at E > −2 V vs. Ag/AgCl).

The intensive interest for graphite [5] for the last four decades was made possible elaborating new reducing materials by potential-controlled ion insertion, especially when using tetraalkylammonium salts (TAA^+X^-), permitting one to reach very negative potentials (<−3 V vs. Ag/AgCl) in aprotic polar solvents. An easy cathodic process leading to almost total exfoliation of graphite by electrochemical insertions of bulky TAA^+ cations was first described in the late 70s [6]. Such graphite exfoliation should yield graphene that is considered as an intriguing poorly soluble redox material. Attempts to prepare single graphene planes via well mastered exfoliation were recently undertaken [7].

The possibilities for graphene (whose plane represents a two-dimensional network of sp^2 carbon atoms) immobilization may be found in its π,π-interactions with basic acceptors that are grafted onto solid (gold) support by conventional means. Recently, a model of insertion of graphene imbedded in the polymer grafted onto GC was proposed [8]. Obviously, the problem of an easy functionalization of solid surfaces with graphene that would not (strongly) alter the properties of this material is still open so that any positive results in this field are of key importance.

A new strategy for fixing graphene (considered as a π-acceptor system) onto glassy carbon could be developed exploiting the fact that the substrate (GC) contains a lot of dispersed graphite and fullerene-like microparticles [1]. An efficient technique for deposition of graphene has been already proposed [8] and GC–graphene structures were successfully used as cathodic interfaces up to rather negative potentials (−2.5 V) without any remarkable swelling–exfoliation process if small radii TAA^+ salts were used. Under such conditions, reproducible charge/discharge processes clearly attributable to deposited graphene were observed, the first step being assigned to the primary redox process of the material. Large possibilities offered by chemical and electrochemical reactions at such three-dimensional systems are evident but we

* Corresponding author.
E-mail address: jacques.simonet@univ-renens1.fr (J. Simonet).

http://dx.doi.org/10.1016/j.elecom.2014.02.007
1388-2481/

intentionally limit the present project to the generation of free radicals arising from carbon–halogen scission (from RX compounds) either in the presence of metal catalysts (e.g., Pd^0 or Au^0) or through the use of activated organic halides on the condition that the applied potential is maintained above −1.5 V to avoid free-radical reduction. As shown hereafter, graphene is associated with GC surfaces as a surface modifier. We chose to build a GC/graphene thin layer doped by metals that are reported to enable electro-catalytic bond scission [9,10] with a large panel of alkyl iodides and activated bromides. Under these conditions, free radicals can be formed, not only at the GC surface, but also within the entire graphene bulk to yield 3D redox materials that may possibly be used as modified electrodes.

The preliminary results reported here show that these conditions can be fulfilled (use of primary alkyl iodides on one hand and of 2-(bromomethyl)pyrene (BMP) on the other hand) allowing deep chemical modification of graphene and building the conducting layers attached to glassy carbon surfaces; thus produced 3D redox material, exhibiting intense electrocatalytic capacity, that may have a great potential for the use in redox catalysis, analysis, and energy-related fields.

2. Experimental section

Electrochemical experiments were carried out in 0.1 M solutions of tetra-*n*-butylammonium tetrafluoroborate ($TBABF_4$), in reagent-grade dimethylformamide (DMF). Experiments described in this work needed no special treatment of electrolytic solutions.

Potentials are referred to the aqueous $Ag/AgCl/KCl_{(sat)}$ system. Voltammetric and coulometric measurements were performed in three-electrode cells separated with a fritted glass. The electrochemical instrumentation has been previously reported [4].

Glassy carbon (GC) electrodes used as substrates for graphene deposition had geometric areas of 0.8 (GC1) and 7 mm^2 (GC3). All glassy carbon samples used as substrates were purchased from Tokai Carbon Co. (code: GC Rod). Graphene was purchased from XG Sciences as XGnP Graphene Nanoplatelets Grade C that typically consist of submicron platelets (particle diameter < 2 μm, with thickness of a few nm). The average surface is of the order of 750 m^2/g and TEM images reveal almost transparent platelets. Oxygen content was reported to be <2 wt.% and that of carbon was >98.0 wt.%. Galvanostatic deposition of transition metals (Pd, Au, Pt and Cu) from the corresponding chlorides (10% aqueous solution) was carried out in 0.1 M HCl passing approximately 10^{-6}C per mm^2 as previously reported [9]. Such a procedure provides ca. 0.5×10^{-9} mol of the metal per square centimeter (apparent geometrical area).

Organic halides (primary alkyl iodides) and BMP were purchased from Aldrich. The synthesis of Fc-$(CH_2)_6$-I was already described [4].

Prior to being modified by deposition of graphene, the electrodes were carefully polished, first with silicon carbide paper {Struers 500} and then with {Struers 1200}. Then, graphene was mechanically disposed on the GC surface by strong pressure rubbing onto a planar surface (glassy cardboard or polished agate) until shiny surfaces were obtained. After these GC–graphene (eventually metallized) structures were used as electrodes for halide reduction (potentiostatic reductions), they were rinsed with water and then with acetone with final drying under a hot air stream (60 °C).

3. Results

Before the voltammetric results specific to RIs at GC/graphene (GC–GR) electrodes are discussed, we show a blank response in Fig. 1, curve A. One observes a reversible first step at −1.75 V, followed by several reproducible steps (specific to the TAAX used) assigned to further charging processes. In the course of the backward scan, several discharge steps are noticed. In the presence of RIs, multi-scan voltammetry (shown for 1-iodopropylbenzene in Fig. 1, curve B) shows a progressive shift (see B1) towards negative potentials, which could suggest progressive alkylation of deposited graphene via its polynucleophilic transient form (Scheme 1, reactions 1 and 2) in a process occurring at the potentials < −1.7 V similar to that already established for GC and graphite [4].

In contrast, when one dopes graphene with very small amounts of metals (Pd, Au, Cu, Ag), a large potential shift towards less negative

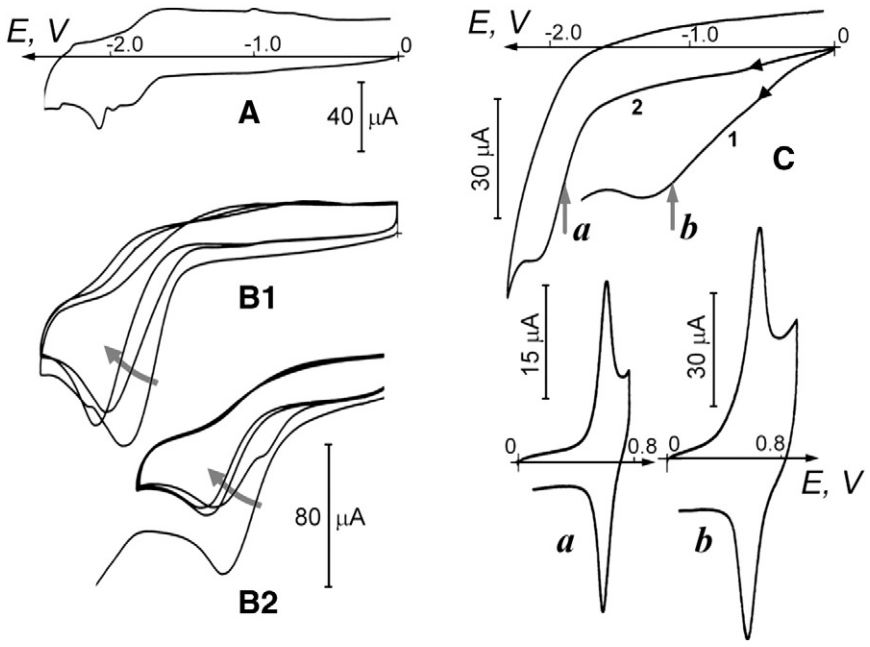
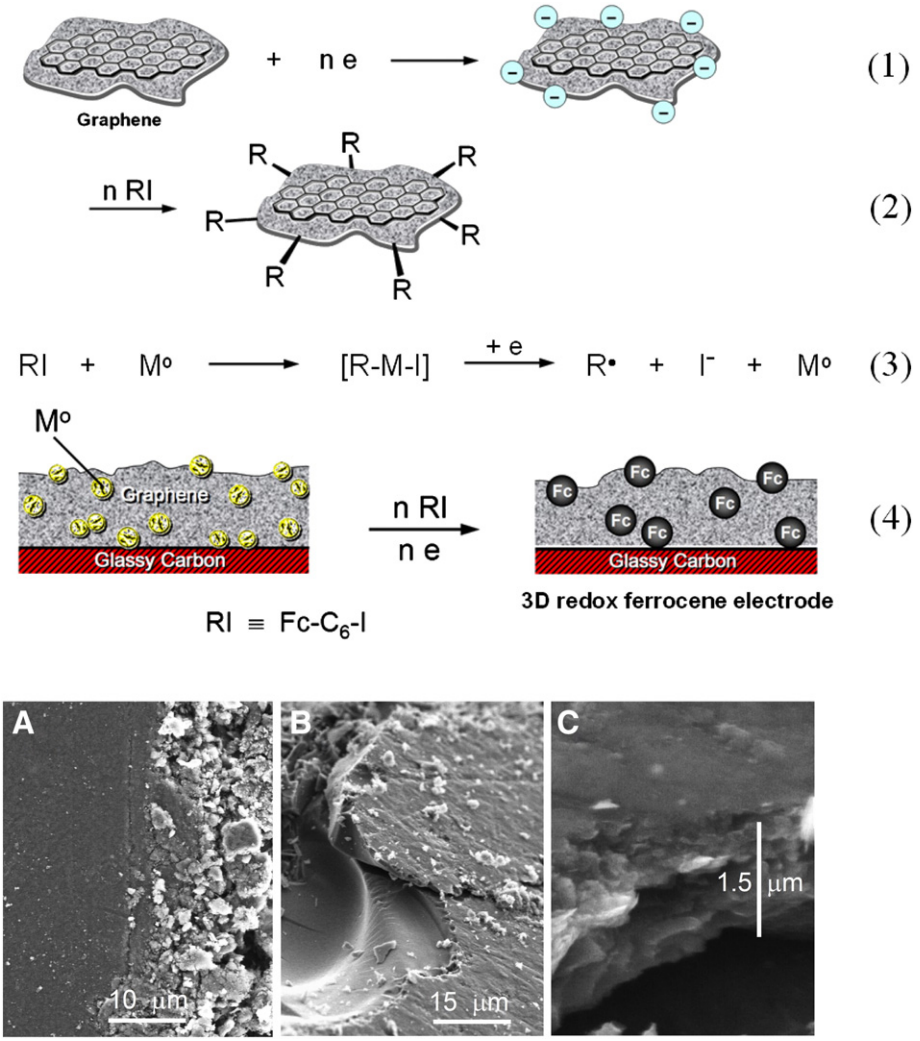


Fig. 1. Voltammetry of RIs at GC and GC–GR electrodes. Scan rate: 50 mV s^{-1}. GC3 electrode. Electrolyte: DMF + $TBABF_4$. (A) Electrochemical response of a GC/graphene electrode. Multi-scan responses of 1-iodopropyl-3-benzene (8.7 mmol L^{-1}) at a GC–GR electrode without (B1) and with (B2) a Pd^0 doping (2×10^{-10} mol cm^{-2}). (C) Voltammetry of 1-iodobutylferrocene (11.3 mmol L^{-1}) at smooth GC (*a*) and at a GC–GR electrode (*b*) doped in volume by Pd^0 (2×10^{-10} mol cm^{-2}). Potential was held for 1 min at the level of arrows (*a*: −1.9 V) and (*b*: −1.1 V); resulting from these graftings, the voltammograms (below, DMF/$TBABF_4$ free of RI) of ferrocene were immobilized within the bulk of graphene layer.



Scheme 1. Nucleophilic (1–2) and radical (3–4) alkylation of graphene and of GC-deposited graphene. Bottom: SEM images of GC–GR interface: (A) Smooth surface with a mechanical scratch on the right, (B) splintered surface, and (C) flank of the graphene layer.

potentials ($\Delta E \approx 0.8$ V) was observed concomitantly with current decay by half in the second scan, suggesting that the reactivity of graphene has fundamentally changed. In fact, free alkyl radicals are now involved in the process because the concerned potential range (around −1 V) corresponds to the zone of relative stability of these species (Scheme 1, reactions 3 and 4). Under these conditions, graphene would appear to be an efficient radical scavenger.

In order to check this, 1-iodopropyl-3-ferrocene (Fc-C_3-I) was investigated both as an electrophile and as a source of free radicals (catalytic one-electron scission in the presence of Pd^0 or Au^0). This proposal was fully verified: without graphenization, smooth GC shows an average coverage by Fc equal to $(3 \pm 2) \times 10^{-9}$ mol cm^{-2}, the value rather compatible with the supposed roughness of the substrate and the nature of the alkylation process [4]. On the contrary, immobilization of ferrocene under the conditions defined in the caption for Fig. 1 is much larger, 2.5×10^{-8} mol cm^{-2}, i.e. 10 times higher. It was checked with Fc-C_6-I that fixed potential electrolyses (at −1 V) with 1.5×10^{-4}C cm^{-2} led to a huge filling of the graphene layer (5×10^{-7} mol cm^{-2}). No attempts, however, were done to test the limit of alkylation.

Benzyl bromides, already reported to generate transient benzyl radicals [11], were also reduced under the conditions developed above. We focus here on the generation of 2-methylpyrene radical from BMP either at GC or at GC–graphene electrodes, eventually in the presence of metal catalysts (Fig. 2). These latter, via oxidative insertion into C–Br bonds promoted in polar solvents, form metalloorganic intermediates whose first reduction step occurs as a one-electron process resulting in C-centered radicals [9].

Thus, BMP is reduced (Fig. 2, curve A) in two steps at a GC–graphene–Pd^0 electrode; the first step corresponds to one-electron cleavage of the C–Br bond in the presence of Pd (reduction of the C–Pd–Br intermediate), and the second shows the one-electron uptake by the pyrene moiety. Amazingly, in the course of the second scan, the first step has vanished. After a potential hold at the level of the first step (generation of free radicals) as depicted in Fig. 2, curve B, an intense reversible step corresponding to the attached pyrene anion radical is obtained. The secondary sharp peak behind the step of embedded pyrene arises from the charge of graphene. The amount of immobilized pyrene within the graphene layers is quite large: 5.4×10^{-8} mol cm^{-2}, which is approximately 10 times the grafting level obtained at a smooth GC electrode (Fig. 2C, curve *b*), for which this value is $(3 \pm 0.5) \times 10^{-9}$ mol cm^{-2}. A first attempt to implement redox catalysis, with the immobilized pyrene radical anion as a surface reducing reagent, is exemplified by curve *b*, Fig. 2. Bromobenzene (curve *a*) is totally indirectly reduced.

4. Conclusion

The generation of free radicals within thin graphene layers deposited onto GC surfaces allows chemical modification of graphene by means of electrophilic reagents, limited here to alkyl halides bearing redox

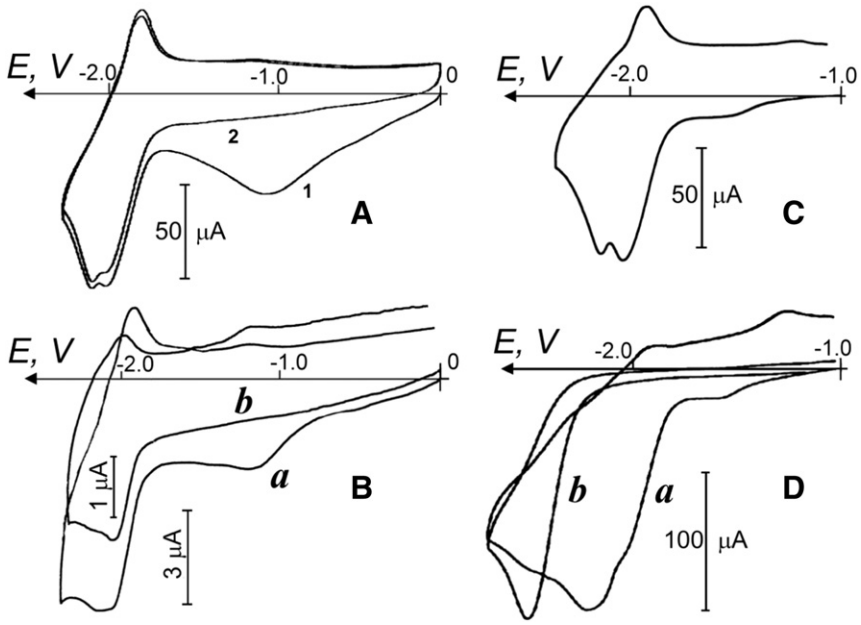


Fig. 2. Voltammetry of BMP at different carbon electrodes (DMF/$TBABF_4$, scan rate: 50 mV s^{-1}). A) Response of BMP at GC–GR doped by Pd^0 (2.1×10^{-1}C cm^{-2}). First and second scans. B) For comparison, voltammetry of BMP (6.6×10^{-3} mol L^{-1}) was drawn at GC1 electrode (curve *a*). In *b*, the response after a potential hold at −1.1 V during 1 min. C) Response after a fixed potential electrolysis (conditions as in A) at −1.0 V (total amount of electricity: 2×10^{-2}C). D) Same electrode as in (C) used as redox electrode for the reduction (a) of bromobenzene (11.2 mmol L^{-1}).

functions. This simple method permits one to build three-dimensional redox interfaces using graphene which, at E > −1.8 V, is essentially perceived as a radical scavenger. The grafting levels are astonishingly high, for the thickness of graphene layers is about 1 μm. Moreover, the stability of such modified electrodes during the successive scans is quite good, presumably because their structure is being held together by π,π-interactions and is quite certainly reinforced by the insertion of poly-aromatic molecules such as pyrene. A proper choice of the function to embed from a very large panel of chemical and organo-metallic functions available allows an (easy) building of a very wide variety of efficient 3D electrodes. The present contribution specifically exemplifies the immobilization of ferrocene and of poly-aromatic groups for building the three-dimensional redox electrodes certainly useful for redox and chemical catalysis. Lastly, intense redox signals produced by such systems appear of great interest for analytical chemistry.

References

[1] R.L. McCreery, Chem. Rev. 108 (2008) 2646.
[2] D.G. Peters, in: H. Lund, O. Hammerich (Eds.), Organic Electrochemistry, M. M. Dekker, New York, Basel, 2001, p. 341.
[3] D. Bélanger, J. Pinson, Chem. Soc. Rev. 40 (2011) 3995.
[4] V. Jouikov, J. Simonet, Langmuir 28 (2012) 931.
[5] K.S. Novoselov, A.K. Geim, S.V. Morozov, D. Jiang, Y. Zhang, S.V. Dubonos, I.V. Grigorieva, A.A. Firsov, Science 306 (2004) 666.
[6] J. Simonet, H. Lund, J. Electroanal. Chem. 75 (1977) 719.
[7] W. Sirisaksoontorn, A.A. Adenuga, V.T. Remcho, M.M. Lerner, J. Am. Chem. Soc. 133 (2011) 12438.
[8] J. Simonet, Electrochem. Commun. 36 (2013) 62.
[9] V. Jouikov, J. Simonet, J. Electrochem. Soc. 160 (2013) G3008.
[10] J. Simonet, V. Jouikov, Electrochem. Commun. 40 (2014) 58.
[11] F. Hui, J.-M. Noel, P. Poizot, P. Hapiot, J. Simonet, Langmuir 27 (2011) 5119.